Indian J. Phys. **52B**, 116-121 (1977)

Infrared spectrum and normal coordinate analysis of tungsten trioxide

L. DIXIT, S. K. KAPOOR, I. D SINGH AND P. L. GUPTA

Indian Institute of Petroleum, Dehra Dun-248005

An attempt has been made to establish the symmetry of tungsten trioxide on the basis of observed absorption bands in the infra red spectra and normal coordinate analysis. Assuming C_{3v} symmetry, observed fundamental bands have been assigned as: ν_1 (A_1) = 1020 cm^{-1}, ν_2 (A_1) = 300 cm^{-1}, ν_3 (E') = 1045 cm^{-1} and ν_4 (E') = 350 cm^{-1}. The results compare fairly well with other isoelectronic systems like MoO_3.

1. INTRODUCTION

The structures of known trioxides which have hitherto been investigated (Herzberg 1945, Schmit and Müller 1974) fall in two categories; those having D_{3h} symmetry such as SO_3, and other having C_{3v} symmetry like MoO_3. Of the first category the molecules have been extensively studied and vibrational spectra and symmetry of several molecules have been established. Vibrational (i.r.) spectrum of MoO_3 has been recently studied by Hewett *et al* (1975) and they have assigned a symmetry C_{3v} to this molecule and have questioned the symmetry of WO_3, which has previously been assigned as D_{3h}. In view of the industrial importance (as catalyst) of WO_3, considerable interest has been shown in the study of spectrostructural aspects of this molecule.

Several authors have attempted the spectrostructural studies of WO_3. McDevitt and Baun (1964) have studied the ir spectra of several solid metal oxides in the 700-240 cm^{-1} region and have reported two poorly defined bands at 355 and 315 cm^{-1} for WO_3 without any assignment. A complete infrared spectrum of solid WO_3 has also been reported by Nyquist and Kogel (1971). Weltner and McLead (1965) have studied the oxides of tungsten in Argon and Neon matrices, and have assigned a band at 1040 cm^{-1} to ν_3 (E') species of WO_3 (D_{3h}) molecule. The assigments of bands at 1024, 874 and 487 cm^{-1} to $(WO_3)_3$ by these authors have been questioned by Hewett *et al* (1975). Comparing the vapour spectra of $(Mo_3)_3$, where M = Mo or W, and taking the planar ring configuration for these polymers, they have predicted that the highest frequency due to trimer or tetramer should lie in the region 950-970 cm^{-1}. In a recent systematic study

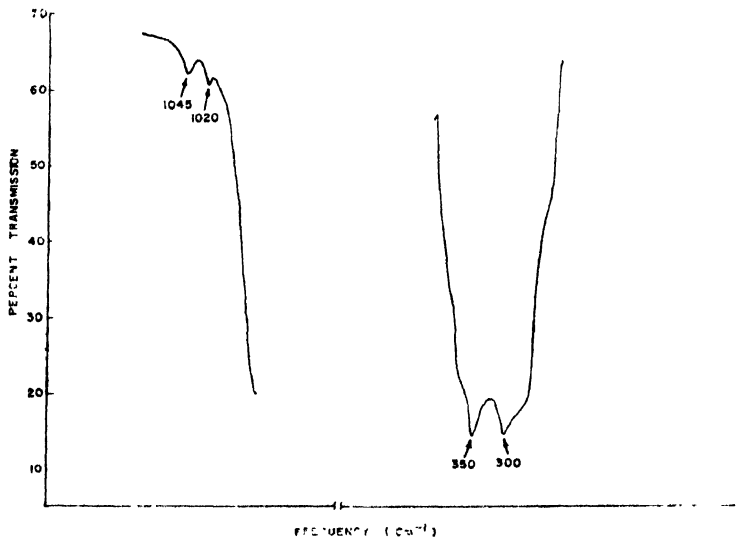
on WO_2, WO_3 and WO_4^{--} systems, Cyvin and Hargittai (1974) have discussed some of the vibrational properties of these systems using vibrational assignments from JANAF Table (1971) and revised the normal coordinate analysis by Nagarajan (1966) for WO_3 (D_{3h}). These authors (Cyvin & Hargettai 1974) have indicated that the estimated ν_1 frequency (564 cm^{-1}) is too low, which is based on the value of a WO stretching force constant. Now with the establishment of a C_{3v} symmetry to MoO_3, which is isoelectronic with WO_3, and doubts raised about symmetry and magnitude of frequencies of WO_3, the present study was initiated to find the vibrational frequencies of WO_3 and to determine whether a C_{3v} configuration may be adopted to explain vibration of WO_3 in agreement with normal coordinate analysis.

2. Experimental

The infrared spectra of WO_3 have been recorded on Beckman IR-12 Double Beam Grating spectrophotometer in the region 200-1200 cm^{-1} using Nujal mull dispersed between CSI plates. The sample was prepared by heating Ammonium Tungstate around 500°C. The spectrophotometer has been calibrated in the whole range using polystyrene and spectroscopically pure Indene.

3. Results and Discussion

The infrared absorption spectrum of WO_3 has been shown in figure 1. Four fundamental absorption bands have been observed at 1045, 1020, 350 and 300 cm^{-1}. The band at 1045 cm^{-1} is very much stronger than that at 1020 cm^{-1}, which appears as a shoulder on the strong absorption due to



polymeric form of WO_3. The intensities of bands at 300 and 350 cm^{-1} are comparable. Table 1 presents the frequencies of WO_3 with assignment together with that of MoO_3 reported earlier.

Table 1. Vibrational frequencies (cm^{-1}) for tungsten trioxide and their comparison with molybdenum trioxide

Species	WO_3		$K_3WO_3F_3$		MoO_3
	Iorns & Stafford (1966)	Present work	Griffiths (1969) I.R	Raman	Hewett et al 1975
$\nu_1(A_1)$	1040	1020 (W) (1021.0)	926 W	931	976 (978.0)
$\nu_1(A_1)$	—	300 (s) (296.7)	322 (s)	328	(260.9)
$\nu_3(E)$	1007	1045 (v.s) (1042.9)	833 (v.s)	828	922.2 (926.1)
$\nu_4(E)$	—	350 (s) (350.7)	322 (s)	328	(275.0)

Values in parentheses are computed

Band Assignment

The vibrational representation of a xy_3 plannar (D_{3h}) molecule is represented as $\Gamma = A_1 + A''_2 + 2E'$, whereas that of a xy_3 pyramidal (C_{3v}) molecule as $\Gamma = 2A_1 + 2E$. Accordingly, in a planar molecule only three freequencies (A_2'' & $2E'$) are i.r. active, while in a pyramidal system all the four frequencies ($2A_1$ & $2E$) should be active in the infrared. In both the systems, the ν_1 and ν_3 stretching modes are expected to occur at higher frequencies than the ν_2 and ν_4 bending deformations. The appearance of two highfrequency infrared bands at 1045 and 1020 cm^{-1} suggests the C_{3v} molecular symmetry for this molecule, which is in consistence with those concluded by Hewett et al (1975) in case of MoO_3. Tse corresponding bands in MoO_{3y} have been observed at 976 and 922.2 cm ^{1}. The assignment of the high frequency fundamentals (stretching modes) can be made on the basis of their relative intensities. For slightly non-planar molecules, one expects the ν_3 (E) mode to be much more intense than the ν_1 (A_1). On this basis we assign the band at 1020 cm ^{1} to be ν_1 (A_1) and that at 1045 cm ^{1} to be ν_3 (E). An analytical expression for the intensity ratio of corresponding symmetric and asymmetric stretching modes has been proposed by Smith (1973) to be A as /As $= \tan^2\beta$ which also confirms the above conclusion with $\beta=62°$. It is worth mentioning that the assignment of 976 cm^{-1} to ν_1 (A_1) and 922.2 cm^{-1}

to ν_3 (E) in case of MoO_3 (Hewett et al 1975) is not justified on the basis of intensity considerations. However, the low frequency ν_2 (A_1) and ν_1 (E) bands are more difficult to assign, as no definite guide-lines exist for intensity and relative magnitudes of the frequencies. In case of MoO_3, the low-frequency bending bands have been computed, assuming a relation $f_\zeta = 0.04$ fr and a constant value of f_γ (0.296 mydne/Å) to be 260.9 and 275 cm^{-1}. It has been observed (Wesley & Dekock 1973) that in case of pyramidal systems ν_2 (A_1) $< \nu_1$ (E). Hence following the assignment of bending modes due to Wesley and DeKock (1973), Lesiecki et al (1972) and Hauge and co-workers (1971), we have assigned ν_2 (A_1) mode to 300 cm^{-1} and ν_4 (E) to 350 cm^{-1} bands. This is in agreement with the asignment ν_2 (A_1) = 260.9 cm^{-1} and ν_4 (E) = 275 cm^{-1} in case of MoO_3.

Normal Coordinate Analysis

Assuming a planar trigonal structure of D_{3h} symmetry for WO_3 molecule, Cyvin and Hargittai (1974) have performed normal coordinate analysis using vibrational frequencies from JANAF Table (1971). Out of four frequencies used in these calculations only one viz. 10 40 cm^{-1} ν_3 (E) has been observed (Wettner et al 1965) in matrix-isolated infrared spectra, while frequencies ν_1 (A_1) at 564 cm^{-1} and ν_2 (A_1) at 347 cm^{-1} have been estimated by Weltner and McLeod (1965) and another ν_4 (E) at 320 cm^{-1} by De Maria *et al* (1960). Here we wish to comment that the assignment of symmetry to a molecule with missing absorption bands is most unreliable. This has also been reflected in the calculation of Cyvin and Hargittai (1974) where the bond-bond interaction force constant, f_{rr}, in case of WO_3 has been reported to be −2.01 mdyne/Å, which is unreasonably high in magnitude. The authors have pointed out that the value af ν_1 (A_1) = 564 cm^{-1} which has been estimated using WO stretching force constant, seems to be too low and thus needs stronger experimental evidence. Based on our assignments described earlier, normal coordinate analysis using Generalized valence force field (GVFF) model described by Nakamoto (1945) has been performed.

Standard F-G matrix method of Wilson has been used to compute intra-molecular force constants within a valence force field discussed by Dixit (1975) and Sanyal and Dixit (1974). The form of kinetic energy matrix is same as described by Nakamoto (1945). The eigenvalues for A_1 and E symmetry species have been solved using $L_{12} = 0$ approximation, which is very well suited to molecule having comparatively low mass-coupling. The description of internal and symmetry coordinates has been shown in figure 2. The angle between two W-O bonds has been found to be 99°45′ using the relationship $\sin \beta = 2/(3)^{1/2} \sin \alpha/2$ where β is the pyramidal angle which has been taken to be 62°. In case of MoO_3, a pyramidal angle of 61.5° has been taken for 1.8 Å MoO bond, and, since a bond length of 1.81 Å for W-O bond has

been used by Cyvin and Hargittai (1974) in case of planar WO_3; we have retained the same (approximately) value of β for WO_3 as that for MoO_3 under constant bond length approximation.

Table 2. Valence force constants (G.V.F.F.) in mydn/A of the trioxides of tungsten and Molybdenum in C_{3v} model

Force constants	MoO_3*	WO_3
f_r	7.46	9.326
f_{rr}	−0.11	−0.025
f_α	0.296	0.477
$f_{\alpha\alpha}$	—	−0.015
$f_{r\alpha}$	—	0.017
$f'_{r\alpha}$	—	0.023

* Valence force constants derived from the symmetry force constant reported by Hewett *et al*, 1975

Table 3. Symmetrized and valence force constants (mdyne/A) of WO_n systems, n = 2, 3, 4, & 6

Systems	Symmetry	F_{11}	F_{22} or F_{33}	f_r	f_{rr}	Ref
WO_2	C_{2v}	8.78	7.27	8.03	0.76	a
WO_3	C_{3v}	9.28	9.34	9.33	−0.02	This work
	D_{3h}	3.80	9.03	7.02	−2.01	a
WO_4^{2-}	T_d	8.17	5.84	6.42	0.58	a
WO_6^{6}	O_h	6.52	3.20	4.10	0.37	b

(a) See Cyvin & Hargittai 1974.

(b) See Ahmad, Dixit & Sanyal 1974.

The symmetry force constants for WO_3 together with that of MoO_3 have been reported in table 2. Table 3 presents the symmetry force constants for WO_3 (C_{3v}) alongwith other WOn systems. From this table, it is observed that the bond strength of W-O decrease regularly increasing number of oxygen atom in WOn system, which is reflected in the form of decreasing magnitude of f_r (W-O). In our calculation, bond-bond interaction force constant, f_{rr} (W-O) comes out to be −0.023 mdyne/Å, and positively represents much stabilized structure (C_{3v}) for WO_3 in contrast to that of

Cyvin and Hargittai (1974) where $f_{r\alpha}$ (W-O) in WO_3 has a value −2.1 mdyne/Å. These approximate symmetry force constants have also been used to compute the stretching and bending frequencies, which compares well with the observed ones (table 1). A more definite assignment of symmetry to WO_3 could be made if the isotopic shift is studied using isotopes of tungsten and/or oxygen.

ACKNOWLEDGMENT

Auhors are thankful to Dr. P. Ratnasamy, I.I.P. for providing the sample and helpful discussion.

REFERENCES

Herzberg, G., 1945 *Infrared and Raman Spectra of Polyatomic molecules De Van* Norstand

Schmit K. H and Müller A., 1974, Coordination Chem. Rev., **14,** 115-179

Hewett, W D Jr, Newton J H, and Weltner, W, Jr 1975, J. Phys Chem **79,** 2640.

McDevitt, N T. and Baun W. L., 1954, Spectrochim Acta, **20,** 799.

Nyquist R. A. and Kagel R. O, 1971 *Infrared Spectra of Inorganic Compounds* Acad Press

Weltner W. Jr. and McLeod, D. Jr, 1965, J. Mol. Spectrosc., **17,** 276

Cyvin S. J. and Hargittai I, 1974, Acta Chim. Acad. Sci Hang (Tomus) **83,** 321-329.

Stull, D R. and Prophet H (Project Directors), 1971, JANAF Thermochemical Tables, 2nd addition. National Bureau of Standards, Washington DC.

Nagarajan, G 1966. Indian J. Pure Appl Phys **4,** 158.

Wesley R D. and Dekock C. W, 1973. J. Phys Chem **77,** 466

Lesiecki, M., Nibler, J. W. and Dekock, C W, 1972. J Chem. Phys **57,** 1352

Haugt, R. H. Hastie, J. W. and Margrave, J. L., 1971. J. less Common metals; **23,** 359.

De Maria G., Burns R. P, Drowart, J and Inghram M. G 1960, J Chem Phys **32,** 1373.

Nakamoto, K. 1945 *Infrared Spectra of inorganic and coordination compounds,* Wiley.

Dixit L. 1975 Ph.D. Thesis, University of Gorakhpur, Gorakhpur. (India)

Sanyal N. K. and Dixit L. (1974) Z. Naturforsch, **29a,** 693-97.

Smit W. M. A., 1973, J. Mol. Structure, **19,** 789.

Ahmad, P. Dixit L and Sanyal M. K 1974, Indian J. Pure Appl Phys. **12,** 489.

Ionns, T. V. and Stafford F. E. (1966), J. Am. Chem Soc **88,** 4819.

Griffiths W. P, 1969 J. Chem. Soc. A 211.